

"MEASUREMENTS AND MODELING OF HYDRATE EQUILIBRIUM CONDITIONS OF SYSTEMS CONTAINING HEAVY HYDRATE FORMERS"

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INTRODUCTION

Gas hydrates were, until recently, considered to be a phenomenon associated with small diameter hydrocarbon molecules. For systems relevant to the oil industry, the upper limit was set by n-butane.

In 1987, Ripmeester et al (1,2) discovered a new hydrate structure called structure H. This structure has cavities larger than those of the former known structures I and II and can therefore be stabilized by heavier guest molecules. Of components found in real hydrocarbon fluids, isopentane, methylcyclopentane, methylcyclohexane and 2,3-dimethylbutane were identified as potential structure H formers while benzene, cyclohexane and cyclopentane were identified as potential structure II formers.

Recently, Thoidi et. al (3) presented experimental and prediction results on the effect of isopentane, methylcyclopentane, cyclopentane and cyclohexane on the hydrate equilibrium properties of two natural gas mixtures. They concluded that structure II heavy hydrate formers increase the hydrate stability of the two hydrocarbon gas mixtures, where as structure H heavy hydrate formers do not have significant effect on the hydrate phase boundary.

In the oil industry the hydrate prevention strategy makes extensive use of hydrate prediction programs. To our knowledge, none of the present commercially available programs take account of the heavy hydrate formers. If some heavy hydrate formers, found in a real hydrocarbon fluid, have a significant effect on the hydrate equilibrium temperature these have to be included in the prediction programs.

In this work the hydrate equilibrium properties of isopentane, cyclopentane and cyclohexane in a synthetic hydrocarbon fluid have been determined. The vapor phase was simulated by either pure methane - a structure I former, or a synthetic gas mixture assuring formation of structure II. The hydrocarbon liquid phase was in all experiments Exxsol D60, which is a paraffinic C9 - C13 distillation cut.

Also presented is a survey of the content of cyclopentane in a selection of real hydrocarbon fluids from the North Sea area.

EXPERIMENTAL

All experiments were performed in a high pressure sapphire PVT-cell. The cell is placed in a temperature controlled air bath in which the temperature can be varied between -40 and +200 °C. The temperature stability is 0.1 °C and the resolution is 0.01°C. The cell has a maximum working pressure of 500 bara. The accuracy of the pressure measurement is estimated to be within 0.5 bar and the resolution is 0.1 bar. The cell volume is controlled and varied using a piston directly coupled to a computerized brushless motor. Volumes are read with a resolution of 0.0001 cm³. The estimated accuracy is 0.005 cm³. Maximum cell volume is 100 cm³.

Stirring is provided by a magnetically coupled stirrer, driven by a computer controlled, variable speed motor. Maximum speed is 1000 rpm. Rheology changes of the experimental fluids are continuously monitored by measurement of the effect required to keep the motor running at constant speed.

Experimental procedures. The sapphire cell was cleaned and evacuated prior to filling of the experimental fluids. All fluids were added gravimetrically in the following sequence: Water (purified by reversed osmosis), hydrocarbon liquid phase (D60 - added various amounts of heavy hydrate formers) and finally the hydrocarbon vapor phase (C1 or synthetic gas mixture). The water cut was, in all experiments, approximately 50%. The hydrocarbon phase were recombined and the saturation point, at ambient temperature, were determined.

Hydrate formation was initiated by cooling the system at a constant rate, 3 - 5 °C/hours, while continuously stirring the cell. After a period of time, allowing for equilibrium to be established, the system was reheated at a rate of 0.25 °C/hours until the hydrates were completely melted. The experiment gives information of the hydrate equilibrium temperature, the degree of sub cooling and the visual appearance of the formed hydrates. Hydrate formation and decomposition are indicated by deflections in a volume vs. temperature plot (the isobar) and by a change in the rheology of the system (the apparent viscosity). The experiments were performed at isobaric conditions, at 100, 200 and 300 bara.

All experiments were documented by video recordings.

Experimental fluids. The synthetic gas mixture were composed of C1, C2 and C3 in the ratio 74.89, 16.47 and 8.64 mole %, respectively. All components were minimum 99.9 % pure. Analysis of the mixture did not show significant contamination of any other components.

Methane were 99.95 % pure. Isopentane, cyclopentane and cyclohexane were all of analytical grade purity.

Exxsol D60 is a commercial paraffinic solvent. The composition of D60 is given in table 1.

The compositions of the different experimental systems are given in tables 2 and 3. The measured saturation pressure and the recombination gas/oil ratio are given along with the composition.

RESULTS AND DISCUSSION

The results from the experiments involving the potential heavy hydrate formers isopentane cyclopentane and cyclohexane, are presented in tables 2 and 3 and figures 1 to 4. Also included in these figures are predictions of the hydrate equilibrium conditions. These predictions were performed by use of PVTsim, a commercially available PVT and phase behavior simulation program.

Isopentane was expected to form structure H while cyclopentane and cyclohexane were expected to form structure II. As can be seen from the figures, only cyclopentane seems to have a significant effect on the hydrate equilibrium conditions for the tested systems. The effect of cyclopentane is, on the other hand, remarkable as hydrate equilibrium temperatures close to 30 °C were observed.

Isopentane: The effect of isopentane is demonstrated in figure 1. As can be seen from this figure, the hydrate equilibrium conditions for the C1/D60 system are not significantly altered by addition of isopentane at a concentration of 9.2 mole %. The C1/D60 system forms a structure I hydrate and our results indicates that, in this system, isopentane do not stabilize either structure II or structure H hydrate.

Cyclopentane: The effects of cyclopentane in a C1/D60 system are presented in figure 2. At concentrations of 9.4 and 4.6 mole % are the equilibrium temperature shifted to higher temperatures and it is reason to assume that the structure is shifted from I to II. At a concentration of 0.9 mole % are the hydrate equilibrium conditions for the C1/D60 system not significantly altered. It can thus be assumed that cyclopentane do not participate in the hydrate formation at this concentration.

The effects of cyclopentane in a synthetic gas/D60 system are presented in figure 3. This system forms structure II also when heavy hydrate formers are not added. The effect of adding 11 mole % cyclopentane to this system is seen by the significant increase in the hydrate equilibrium temperature.

Addition of 1.1 mole % cyclopentane to the synthetic gas system gives only a marginal increase (0.2 °C) of the hydrate equilibrium temperature.

Cyclohexane. The results from the experiments involving cyclohexane in a C1/D60 system are presented in figure 4. There were not observed any stabilizing effects in this system, which is expected to form structure I when no heavy hydrate formers are added. It seems therefore reasonable to conclude that cyclohexane, at this concentration, do not stabilize either structure II or structure H.

Significance for the hydrate prevention strategy. Figure 2 and 3 clearly states that cyclopentane at concentrations of 9.4 and 4.6 mole % significantly increases the hydrate equilibrium temperatures. 1.0 mole % cyclopentane has, on the other hand, no significant impact on the hydrate equilibrium.

For the two systems tested, C1/D60 and synthetic gas/D60, our hydrate prediction program PVTsim predicts structure I and II, respectively. Cyclopentane is not included as a hydrate former in this program and the only predicted effect of adding cyclopentane to the test systems are a dilution of the hydrate formers and thus a slight reduction of the hydrate formation temperatures. At higher concentrations of cyclopentane will this clearly lead to a significant miscalculation of the hydrate equilibrium conditions.

Neither the concentration at which cyclopentane is able to switch from structure I to structure II, nor the concentration at which cyclopentane is able to significantly change the equilibrium temperature of structure II hydrate, are known. It seems, however, that 0.9 - 1.1 mole % is below the critical concentration where cyclopentane affect the hydrate equilibrium.

A survey of the content of cyclopentane in a selection of North Sea oil is given in table 4. As can be seen from this table the concentration seems, in general, to be below the critical concentration for having any significant impact on the hydrate equilibrium conditions.

CONCLUSIONS

- 1 The hydrate formation characteristics of two synthetic hydrocarbon system containing three heavy hydrate formers have been investigated.
- 2 9.2 mole % isopentane do not promote formation of structure II or structure H in a methane/D60 system. The hydrate equilibrium conditions are not significantly influenced.
- 3 9.4 and 4.6 mole % cyclopentane promotes formation of hydrate structure II in both the methane/D60 system and the synthetic gas/D60 system. The hydrate equilibrium conditions were shifted to higher temperatures.
- 4 1.0 mole % cyclopentane do not change the hydrate structure from I to II in the methane/D60 system and do not significantly increase hydrate the stability of structure II in the synthetic gas/D60 system.
- 5 8.0 mole % cyclohexane in a methane/D60 system do not promote formation of hydrate structure II or structure H and do not affect the hydrate equilibrium conditions.
- 6 In 13 different North Sea oil surveyed, are the concentrations of cyclopentane too low to affect the hydrate stability. We believe that the hydrate equilibrium conditions, for these oils, can be predicted with reasonable accuracy.

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Table 1. Composition and properties of Exxsol D60.

Carbon no.	C9	C10	C11	C12	C13
N + iso paraffin (wt. %)	0	5	23	23	6
Naphtenes (wt. %)	1	13	18	8	3
Mw	126.2	140.8	155.4	169.8	183.7
Density (kg/m ³)	768	778	788	797	805

Table 2. The synthetic gas/D60 system. Composition and hydrate equilibrium data.

System	S.0	S.1	S.2
C1 (mole %)	41.16	38.02	39.9
C2 (mole %)	9.05	8.36	8.78
C3 (mole %)	4.75	4.39	4.60
Cy-C5 (mole %)		10.97	1.07
D60 (mole %)	45.03	38.26	45.66
GOR (Sm ³ /Sm ³)	144	139	132
Psat (Bara)	131 @23.1 °C	125 @23.9 °C	141@29°C
Hydrate equilibrium (°C):			
@ 100 Bara	19.7	25.3	19.9
@ 200 Bara	22.0	27.4	22.2

Table 3. The methane/D60 system. Composition and hydrate equilibrium data.

System	C.0	C.1	C.3
C1 (mole %)	60.87	57.69	57.67
i-C5 (mole %)		9.22	
Cy-C5 (mole %)			9.43
D60 (mole %)	39.13	33.09	32.90
GOR (Sm ³ /Sm ³)	182	182	183
Psat (Bara)	253 @24 °C	227 @23.6 °C	228 @24.5 °C
Hydrate equilibrium (°C):			
@ 100 Bara	13.7	12.9	25.7
@ 200 Bara			29.4
@ 300 Bara			29.8

Table 3 cont. The methane/D60 system. Composition and hydrate equilibrium data.

System		C.4	C.5	C.6
C1	(mole %)	59.02	59.75	58.47
C2	(mole %)			
Cy-C5	(mole %)	4.61	0.92	
Cy-C6	(mole %)			8.01
D60	(mole %)	36.37	39.33	33.52
GOR	(Sm ³ /Sm ³)	180	176	182
Psat	(Bara)	247 @25.4 °C	247 @21.7 °C	244 @24 °C
Hydrate equilibrium (°C):				
@ 100 Bara		22.4	13.1	13.6
@ 200 Bara			18.6	
@ 300 Bara			20.9	

Table 4. Content of cyclopentane in North sea oils.

Oil I.D.	Cyclopentane (mole %)	Cyclopentane (wt %)
1	0.04	0.01
2	0.03	0.01
3	0.07	0.05
4	0.07	0.05
5	0.12	0.11
6	0.04	0.04
7	0.05	0.04
8	0.06	0.05
9	0.05	0.04
10	0.09	0.09
11	0.08	0.08
12	0.04	0.02
13	0.07	0.03

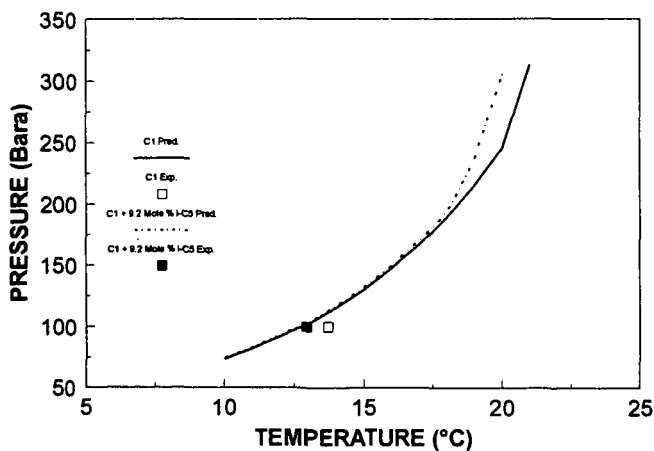


Figure 1. Experimental and predicted hydrate equilibrium conditions for a methane/D60 system containing isopentane.

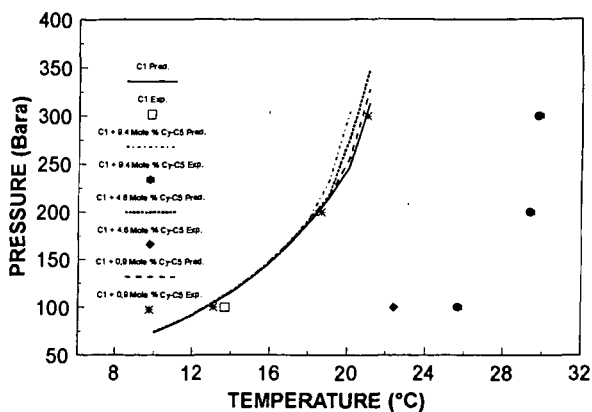


Figure 2. Experimental and predicted hydrate equilibrium conditions for a methane/D60 system containing cyclopentane.

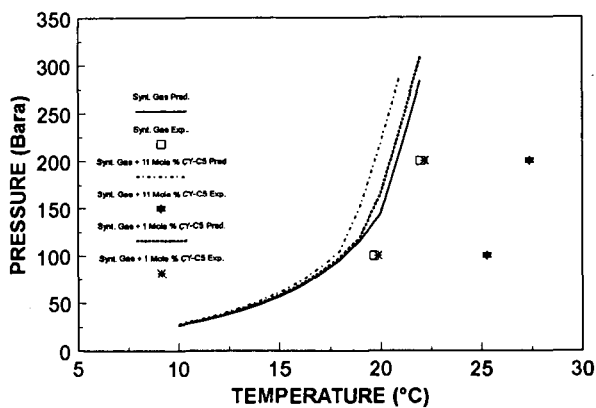


Figure 3. Experimental and predicted hydrate equilibrium conditions for a synthetic gas/D60 system containing cyclopentane.

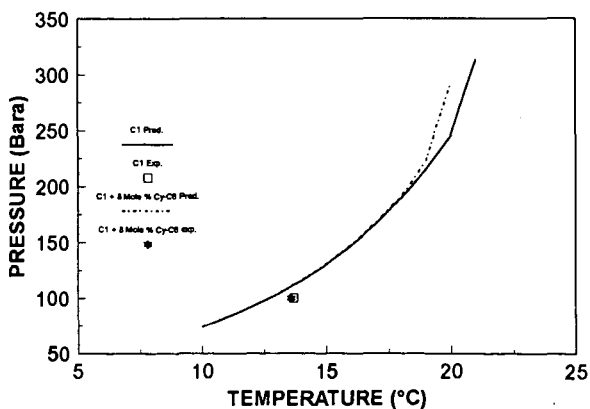


Figure 4. Experimental and predicted hydrate equilibrium conditions for a methane/D60 system containing cyclohexane.